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CHLORIDE MIGRATION IN CONCRETE WITH SUPERABSORBENT POLYMERS

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Abstract

Superabsorbent polymers (SAP) can be used as a means for internal curing of concrete. In the present study, the development of transport properties of concrete with SAP is investigated. The chloride migration coefficient according to NT BUILD 492 is used as a measure of this. Twenty concrete mixtures are tested 7, 14, and 28 days after casting. The development of degree of hydration is followed for 20 corresponding paste mixtures.

Both when SAP is added with extra water to compensate the SAP water absorption in fresh concrete and without extra water, the internal curing water held by SAP may contribute to increase the degree of hydration. No matter if SAP is added with or without extra water, it appears that the so-called gel space ratio can be used as a key parameter to link age and mixture proportions (water-to-cement ratio and SAP dosage) to the resulting chloride migration coefficient; the higher the volume

of gel solid relative to the space available for it, the lower the chloride migration coefficient, because the pore system becomes more tortuous and the porosity becomes less.

Keywords:

Concrete; Superabsorbent polymer (SAP); Internal curing; Chloride migration; Microstructure; Transport

1. Introduction

Superabsorbent polymer (SAP) has been introduced in concrete mix design as a means for internal water curing of cementitious materials with low water-to-cement (w/c) ratios to mitigate autogenous shrinkage [1, 2]. However, before SAP can be used in concrete production on a larger scale, it is important to clarify not only how SAP influences autogenous shrinkage, but also how it influences other concrete properties.

Concrete is a material with open porosity, and for this reason there is a possibility of transport through the pore system. Transport of matter is often involved in the deterioration of concrete. For example, the diffusion of chloride ions has implications for reinforcement corrosion, and the change of moisture content can lead to frost damage, if the concrete is exposed to sub-zero temperatures. Despite the importance of transport, the influence of SAP on transport properties in general and chloride transport in particular has only been superficially examined. In a recent state-of-the-art report [3], the presented results regarding chloride migration comprises only 4 concrete mixtures with SAP. The 4 concrete mixtures represent 2 different w/c ratios, 2 different types of SAP, and different SAP sizes, and according to the authors, it is not possible to deduce a final conclusion on how SAP influences chloride migration. The authors of the present paper are not aware of other data published.

SAP addition can influence cement hydration, as the cement paste can imbibe water from a swelled SAP particle, if water within the paste itself becomes in short supply. The objective of the present study is to link development of transport properties and cement hydration through a systematic study of both parameters. Chloride migration is used as a measure of transport. In real concrete structures, e.g. structures in marine environment, chloride transport often takes place as a diffusion

process. Measurements of chloride transport can be seen as an indication of how the concrete will sustain ingress of other substances, where the transport is driven by a concentration gradient. The methodology, where a specific property is assumed to be the result of cement hydration and therefore can be modelled as a function of degree of hydration has been successfully applied for other concrete properties [4, 5].

2. Theory

2.1 Powers' model

In 1948, Powers and Brownyard published results showing that when 100 g of cement hydrates, then 23 g of water is bound chemically in the gel solid, and 19 g of water is bound by physical adsorption on the gel solid surfaces [6]. The adsorbed water phase is called gel water. Powers and Brownyard also showed that cement hydration is followed by chemical shrinkage: when 100 g of cement fully hydrates, the volume of the resulting gel solid and gel water is 6.4 ml smaller than the volume of cement and water before hydration. In this way, the distribution of phases in the hardening cement paste depends linearly on the degree of hydration, see equations 1a-1e:

$$V_{cs} = 64 \cdot 10^{-6} \cdot \rho_c (1-p) \alpha \quad (1a)$$

$$V_{cw} = p - (0.19 + 0.23) \left(\frac{\rho_c}{\rho_w} \right) (1-p) \alpha \quad (1b)$$

$$V_{gw} = 0.19 \cdot \left(\frac{\rho_c}{\rho_w} \right) (1-p) \alpha \quad (1c)$$

$$V_{gs} = \left(1 - 64 \cdot 10^{-6} \cdot \rho_c + 0.23 \cdot \left(\frac{\rho_c}{\rho_w} \right) \right) (1 - p) \alpha \quad (1d)$$

$$V_{uc} = (1 - p)(1 - \alpha) \quad (1e)$$

where

- V is the relative volume fraction specified by the subscript: cs = chemical shrinkage; cw = capillary water; gw = gel water; gs = gel solid; uc = unhydrated cement [m³/m³ cement paste]
- ρ_c and ρ_w are densities of cement and water, respectively [kg/m³]
- α is the degree of hydration [-]
- p is the initial porosity, i.e. the volume fraction of capillary water at $\alpha = 0$,

$$p = (w/c) / \left((w/c) + \left(\rho_w / \rho_c \right) \right) [-]$$

The essence of equations 1a-1e can be presented graphically, see figure 1 (left). The model is known as Powers' model. This model predicts that if cement paste with w/c ratio lower than 0.42 hydrates in sealed conditions, complete hydration is not possible, i.e. the maximum degree of hydration $\alpha_{max} < 1$.

Figure 1 (right) illustrates how Powers' model can be extended to account for entrained water [1], e.g. water which in the fresh cement paste is present in swollen SAPs. For cement paste in sealed conditions with w/c ratio lower than 0.42, access to an entrained water source increases α_{max} .

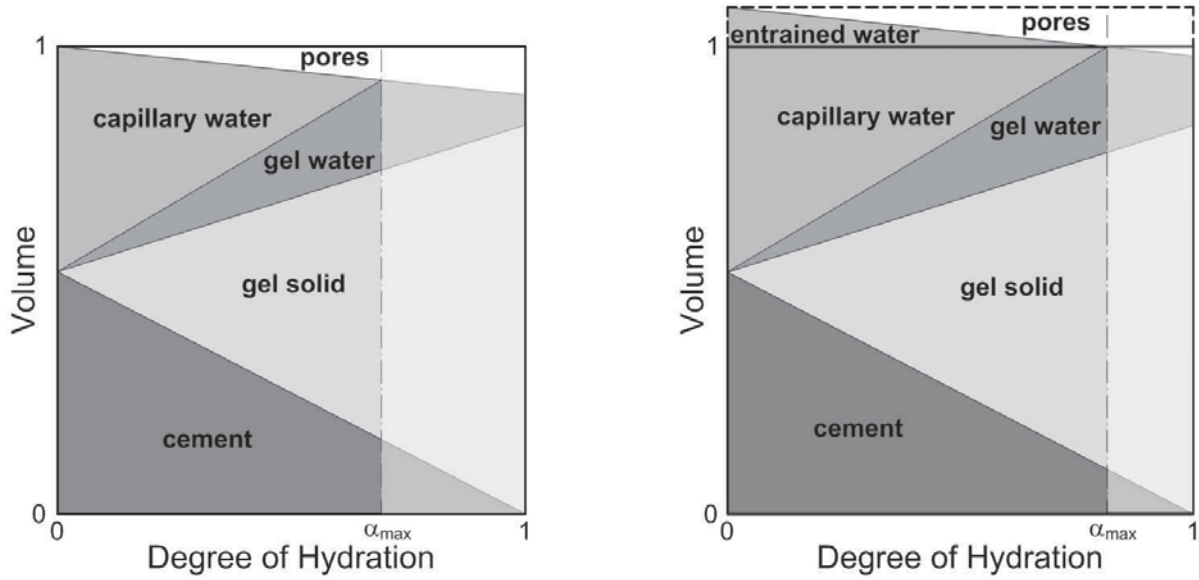


Figure 1: Powers' model for cement hydration in sealed conditions. Left: w/c ratio = 0.30. Right: w/c ratio = 0.30, entrained water $w_e/c = 0.05$. Illustrations are taken from [1].

2.2 SAP influence on transport properties

It is difficult prior to experiments to forecast if SAP addition will increase or reduce chloride transport in concrete. On one hand, if SAP addition increases the maximum degree of hydration, the paste phase will be more dense due to a higher amount of gel solids; the capillary pore network will be more tortuous and there will be more cut-offs of connections between capillary pores. This suggests that ion transport is reduced. On the other hand, if as assumed in figure 1 (right), water from SAP will fill up pore space created by chemical shrinkage that would otherwise be empty, then SAP addition leads to a higher amount of capillary water. Moreover, without the empty spaces, the capillary water will form a more or less continuous phase. As ion transport mainly takes place in capillary water and only to a limited extent in gel water, this may suggest that SAP addition will increase ion transport.

1 There may also be an effect of the voids created by SAP, and again there are 2 possibilities: If the
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3 SAP voids are empty, ions have to travel a slightly longer route to pass the void. This is similar to
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5 the effect of dense aggregates in mortar and concrete, as ion transport does not go through the stone
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7 materials. As regards aggregates, this effect has been shown to be small [7]. But if SAP voids are
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9 filled with liquid, they may provide an expressway without obstacles for ion transport. However,
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11 the liquid in the void may be wholly or partly held within a swelled SAP particle and the transport
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13 properties in a swelled SAP particle are not known. It is likely that transport will be slower than in
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15 liquid not held by SAP, just as transport has been shown to be slower, if a viscosity modifying agent
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17 has been added to the liquid [8].
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27 **3. Materials and methods**

31 **3.1 Test specimens**

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33 The test program is based on 3 reference concrete mixtures without SAP, see table 1. The mixtures
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35 are laboratory mixtures suitable for research purposes, where it is the intention to have as few
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37 variables as possible. This is for example the reason why high range water reducing agents
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39 (HRWRA) have not been used in some of the stiffer mixes: HRWRAs may have a retarding effect
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41 and thereby introduce a new variable that has to be taken into account.
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Table 1: Mix design for reference concretes and examples of mix design for concrete with SAP. All values are stated as [kg/m³ concrete]. For aggregates, the amounts refer to their saturated, surface dry state. Volume of air voids has not been taken into account.

Constituent	Reference mixes			Example 1:	Example 2:
	w/c 0.35	w/c 0.40	w/c 0.50	Starting point: w/c = 0.35 + 0.2 % SAP (no extra water)	Starting point: w/c = 0.35 + 0.2 % SAP + extra water
Cement [†]	552	514	451	552	552
Water	193	205	225	193	193+14=207
SAP ^{††}	-	-	-	1.1	1.1
Sand	831	831	831	830	811
Coarse aggregate, 4-8 mm	166	166	166	166	162
Coarse aggregate, 8-11 mm	665	665	665	664	648
w/c ^{†††}	0.35	0.40	0.50	0.325	0.350
w/c entrained ^{†††}	-	-	-	0.025	0.025
w/c total	0.35	0.40	0.50	0.350	0.375
<hr/>					
†	Aalborg Portland Rapid [®] (CEM I 52.5 N (MS/LA/<2))				
††	Suspension-polymerized covalently cross-linked acrylamide/acrylic acid copolymer. Amount stated is amount of dry SAP. It is assumed that when this SAP is mixed in concrete, 1 g SAP absorbs 12.5 g water.				
†††	“w/c” is the w/c ratio of the cement paste in fresh concrete, after SAP has absorbed part of the mixing water. “w/c entrained” refers to the amount of water present in the swollen SAP in the fresh concrete.				

The reference mixtures are chosen so they all have the same paste content (37% of concrete volume), and at the same time workability is acceptable for all mixtures, though the concrete becomes stiffer as the w/c ratio decreases. For each w/c ratio, 4 mixtures are prepared with different amounts of SAP (0.05, 0.1, 0.2 and 0.3 % relative to cement mass) without adding extra water, see example 1 in table 1. Moreover, 2 mixtures are prepared for each w/c ratio with 0.2 % and 0.6 % SAP, where extra water is added to account for the amount of water absorbed by SAP (only 0.6 % is tested for the w/c ratio of 0.40), see example 2 in table 1. In both cases, the volume of dry SAP and possible extra water replaces an equivalent volume of aggregates. In all mixtures, the aggregate composition based on mass $m_{\text{sand}}:m_{4-8 \text{ mm}}:m_{8-11 \text{ mm}}$ is maintained at 50:10:40.

Before the mixing of each concrete mixture, the actual moisture content of the aggregates is measured by drying aggregate samples in a microwave oven until constant mass is reached. The amount of mixing water is adjusted, if the moisture content differs from the moisture content corresponding to the saturated, surface dry condition of the aggregates. The concrete is mixed in a 60 L pan mixer: First 2 minutes mixing of dry constituents, then addition of mixing water followed by 4 minutes of mixing. The concrete is cast in cylinders ($\varnothing 100 \text{ mm} \times 200 \text{ mm}$) on a vibrating table.

Paste mixtures are prepared in a standard Hobart mixer (mixing time: 4 minutes). The paste is immediately cast in cylindrical moulds ($\varnothing 14 \text{ mm} \times 70 \text{ mm}$), using a small vibrating table when necessary. The specimens are rotated in a rotary machine for 24 h to avoid bleeding.

Both concrete specimens and paste specimens are demoulded 24 h after mixing, tightly sealed in weldable aluminium-plastic wrapping foil, and stored at 20 °C until testing.

3.2 Test methods

3.2.1 Fresh concrete properties

For all fresh concrete mixtures, the slump and the total air content is measured according to EuroNorm methods [9, 10]. This is primarily done as a quality control measure.

3.2.2 Chloride migration

The chloride migration coefficient is measured according to NT BUILD 492 [11]. The scope of this method is that at the time of testing, a 50 mm disc sawn from a Ø100 mm cylinder is first vacuum saturated in limewater and then placed in a set-up, where it is exposed to an aqueous 10 % NaCl solution on one side and a 0.3 mol/L NaOH solution on the other side. A DC power supply is connected with the cathode in the NaCl solution and the anode in the NaOH solution. The set-up used is shown in figure 2.

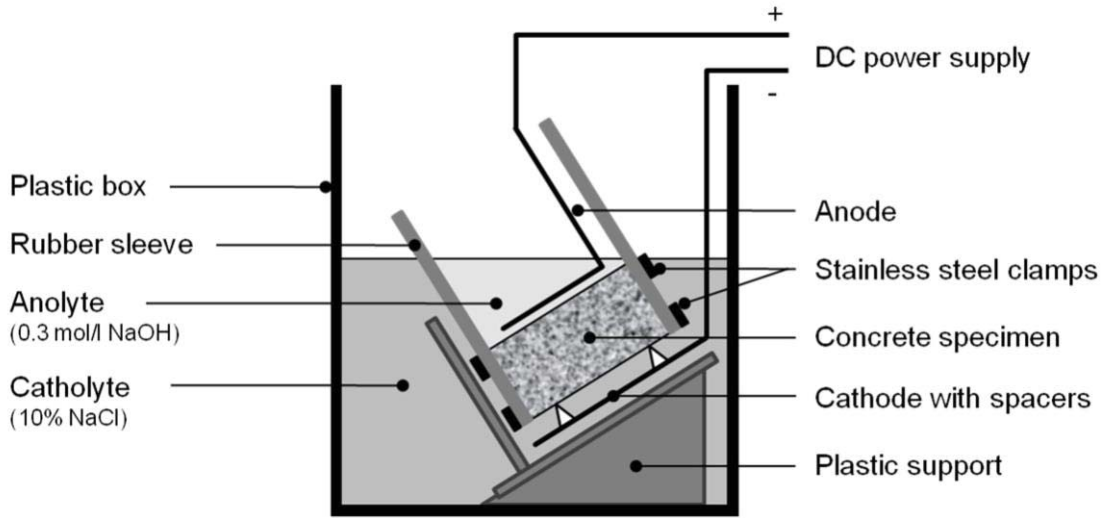


Figure 2: Experimental set-up according to NT BUILD 492.

The electrical field forces the negative Cl^- ions to migrate into the concrete. The voltage and test duration depends on the concrete quality; 24 h is applicable for most concrete qualities. After the voltage is terminated, the specimen is split lengthwise in half and the chloride ingress front is made visible for measurement by spraying the fresh fracture surface with silver nitrate solution (0.1 mol/L). The chloride penetration depth is measured at seven locations on the fracture surface; one at the centre of the specimen and three at each side of the centre, with 10 mm between locations. When calculating the average penetration depth, measurements where the chloride front is clearly blocked by an aggregate particle are omitted from the calculation.

Given the experimental circumstances – concentrations of anolyte and catholyte, etc. – the non-steady-state migration coefficient D_{nssm} can be calculated according to equation (2) [11]:

$$D_{nssm} = \frac{0.0239 \cdot (273 + T) \cdot L}{(U - 2) \cdot t} \cdot \left(x_d - 0.0238 \sqrt{\frac{(273 + T) \cdot L \cdot x_d}{U - 2}} \right) \cdot 10^{-12} \quad (2)$$

where

- D_{nssm} is the non-steady-state migration coefficient [m²/s]
- U is the absolute value of the applied voltage [V]
- T is the temperature (measured as average of initial and final temperature in the anolyte) [°C]
- L is the thickness of the specimen [mm]
- x_d is the average chloride penetration depth for the specimen [mm]
- t is the test duration [h]

Each measurement is made in triplicate, i.e. the non-steady-state migration coefficient D_{nssm} for a specific concrete mixture at a specific time is the average of measurements for 3 specimens.

This method is chosen, because the test duration is relatively short; it takes approximately 48 h to measure the chloride migration coefficient from the beginning of the saturation process to the end of chloride exposure. Methods, where the test specimen is immersed in saline solution and then the diffusion coefficient is determined based on a chloride profile typically takes several months to perform, and then it is difficult to assign the measured value to a certain concrete age; what is measured will represent a kind of average of the transport property during the period of testing.

The NT BUILD 492 test method can be used to elucidate how transport properties are influenced by SAP due to changes of the solid structure of the concrete caused by SAP. But as the specimens are artificially saturated, this method cannot show the influence of e.g. change in moisture state or void structure.

3.2.3 Degree of hydration

The degree of hydration is measured according to a non-standardised method:

1. At the time of testing, the paste sample is unwrapped and part of the paste cylinder (~ 10 g) is immediately crushed and weighed (m_1).
2. The crushed sample is vacuum dried for 1 h (this step can be omitted, but vacuum drying quickly lowers the relative humidity of the sample and thereby stops further hydration, so by applying this step, the time for end of hydration becomes more precise).
3. The sample is then dried 24 h at 105 °C, and weighed (m_2) to determine the amount of evaporable water, i.e. the sum of gel water and capillary water ($m_1 - m_2$).
4. Finally, the sample is heated at 1050 °C for 1 h, and weighed (m_3).

Assuming that the mass change during heating at 1050 °C (step 4) solely is due to release of chemically bound water, and that what is left after heating equals the mass of cement in the sample, then the degree of hydration can be calculated in the following way, see equation 3:

$$\alpha = \frac{m_{cw}}{0.23 \cdot m_c} = \frac{m_2 - m_3}{0.23 \cdot m_3} \quad (3)$$

where m_c and m_{cw} are masses of cement and chemically bound water, respectively.

However, the mass difference before and after heating at 1050 °C is not entirely due to loss of water chemically bound during hydration. The cement contains gypsum and limestone filler. Water chemically bound in gypsum and CO₂ bound in limestone filler are both released during heating to 1050 °C. They are the primary reasons for cement loss on ignition (*LOI*). The *LOI* of cement has been measured: 2.8 %. The degree of hydration is overestimated, if the *LOI* of cement is not taken into account. The correction is made in the following way, see equation 4.

$$\alpha = \frac{m_{cw}}{0.23 \cdot m_c} = \frac{m_2 - m_3 / (1 - LOI)}{0.23 \cdot m_3 / (1 - LOI)} \quad (4)$$

SAP is an organic compound that undergoes combustion during heating at 1050 °C. *LOI* of the SAP used in this study is 88.2 %. The *LOI* for a combination of cement and SAP can be calculated, when the SAP content is known.

Measurements of chloride migration coefficient and degree of hydration are carried out at 7, 14, and 28 days after mixing.

4. Results

The air content is for all mixtures in the range 0.2 % to 2.8 % (natural or entrapped air content). There tends to be a higher air content in mixtures with low *w/c* ratio, probably because the mixture is stiffer and therefore more easily entraps air.

Results for degree of hydration are shown in figure 3. The presented results are calculated according to equation (4), taking *LOI* of cement and SAP into account.

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Measured chloride migration coefficients are shown in figure 4.

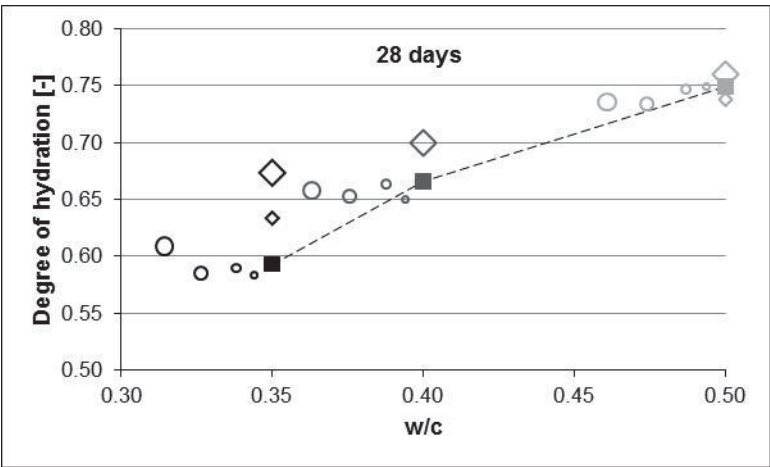
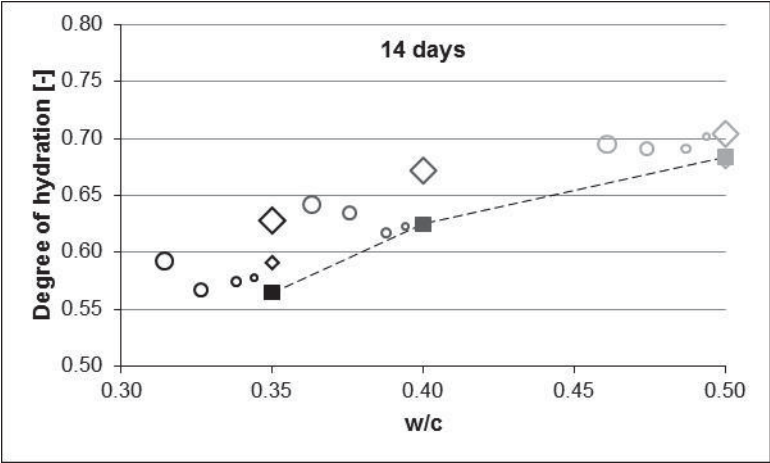
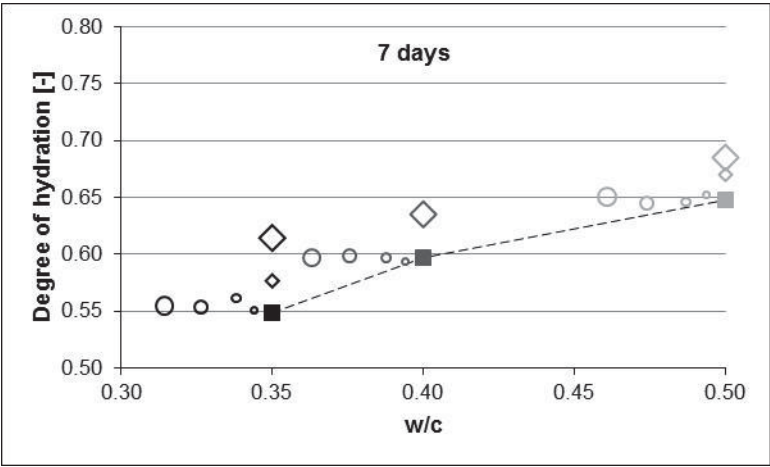


Figure 3: Degree of hydration vs. w/c ratio (w/c is defined in table 1, note 3) at 3 different ages.

Explanation of symbols: Reference mixture: ■. Mixture, where SAP is added without extra water:
○. Mixture, where SAP is added with extra water: ◇. Size of circle or diamond represents amount of
SAP.

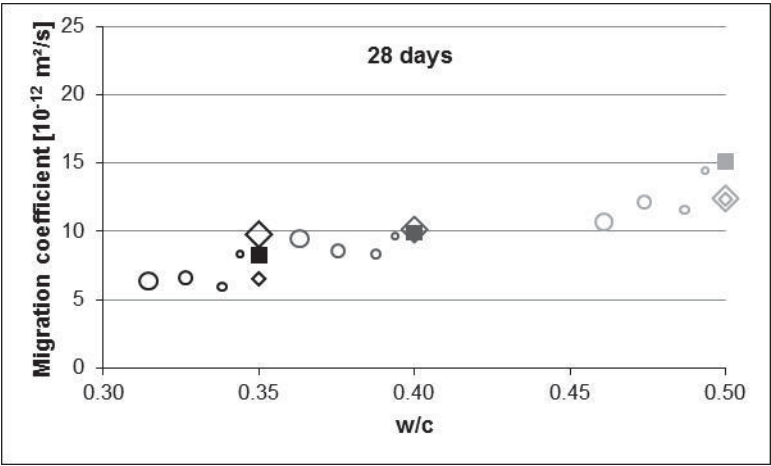
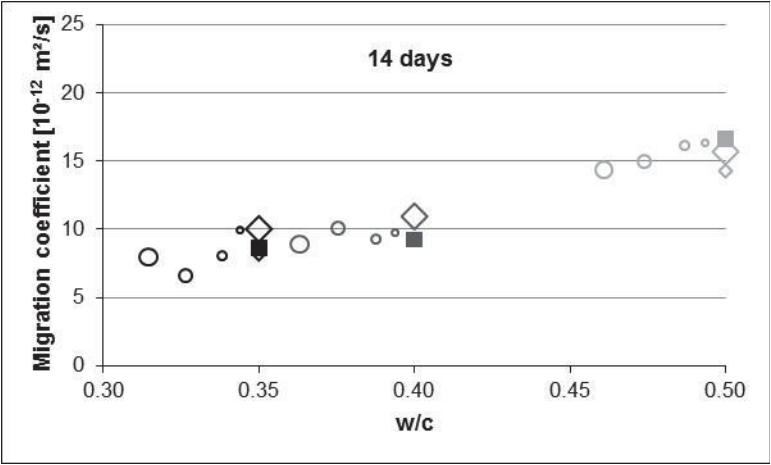
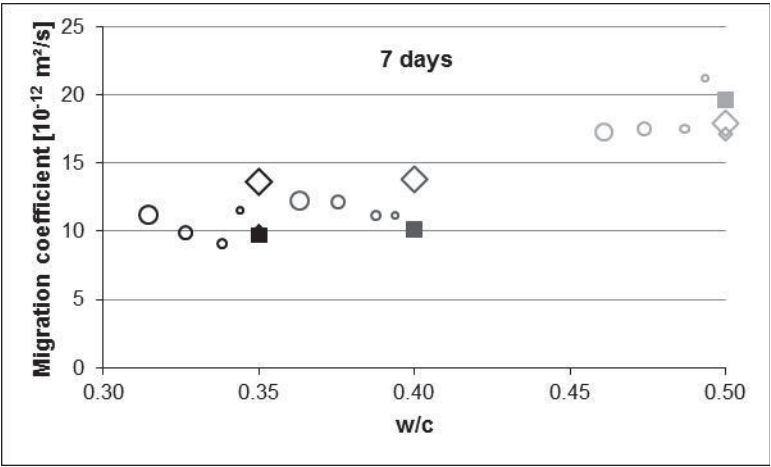


Figure 4: Chloride migration coefficient D_{nssm} vs. w/c ratio (w/c is defined in table 1, note 3) at 3 different ages. The same legend is used as in figure 3.

5. Discussion

5.1 Degree of hydration

Figure 3 shows that for all mixtures the degree of hydration increases with age, as expected. For mixtures where SAP is added together with extra water, the degree of hydration is higher than for the reference mixtures (except for $w/c = 0.50$ at 28 days). For mixtures where SAP is added without extra water, the degree of hydration seems to follow the reference mixture, though the mixtures have different initial w/c ratio in the paste phase following absorption of water by the SAP. This is even more clearly seen in figure 5, where the degree of hydration is plotted as a function of total w/c ratio:

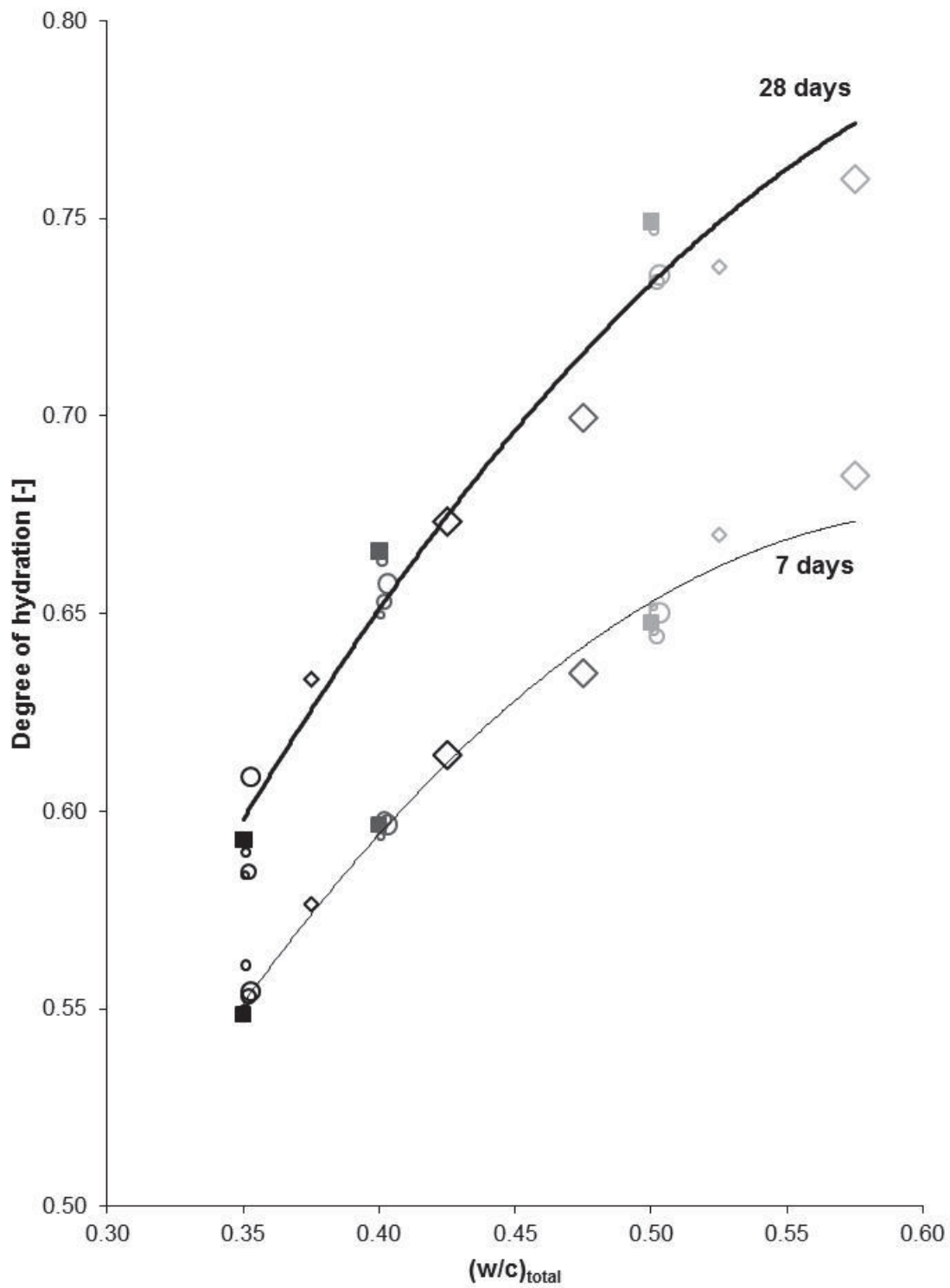


Figure 5: Degree of hydration vs. $(w/c)_{total}$ at 7 days and 28 days, respectively. The same legend is used as in figure 3.

1 In Figure 5, trend lines for 7 and 28 days, respectively, are quadric functions fitted through (0,0),
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3 i.e. polynomials of the form $A \cdot x^2 + B \cdot x$. This gives a soft curve and is physically meaningful in the
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5 sense that the degree of hydration shall be 0 at all ages for $w/c = 0$. However, it is only meaningful
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7 up to the vertex of the curve as the degree of hydration does not drop again for w/c ratios higher
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9 than a certain value.
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16 In a previous study [4], development in degree of hydration was measured from earlier ages than in
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18 the present one. Results from [4] are plotted in the same way as in figure 5, see figure 6. In [4], 3
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20 reference mixtures were used with w/c ratio 0.35, 0.40, and 0.50, respectively, and for all w/c ratios,
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22 5 mixtures with different SAP dosages were prepared (0 % to 0.6 % of cement mass). In all
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24 mixtures with SAP, extra water was added to compensate for SAP absorption. Experimental
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26 investigations were performed with the same type of cement and same type of SAP as in the present
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28 study, but specimens were stored at 25 °C, so results for the same age, e.g. 28 days, are not directly
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30 comparable due to maturity differences.
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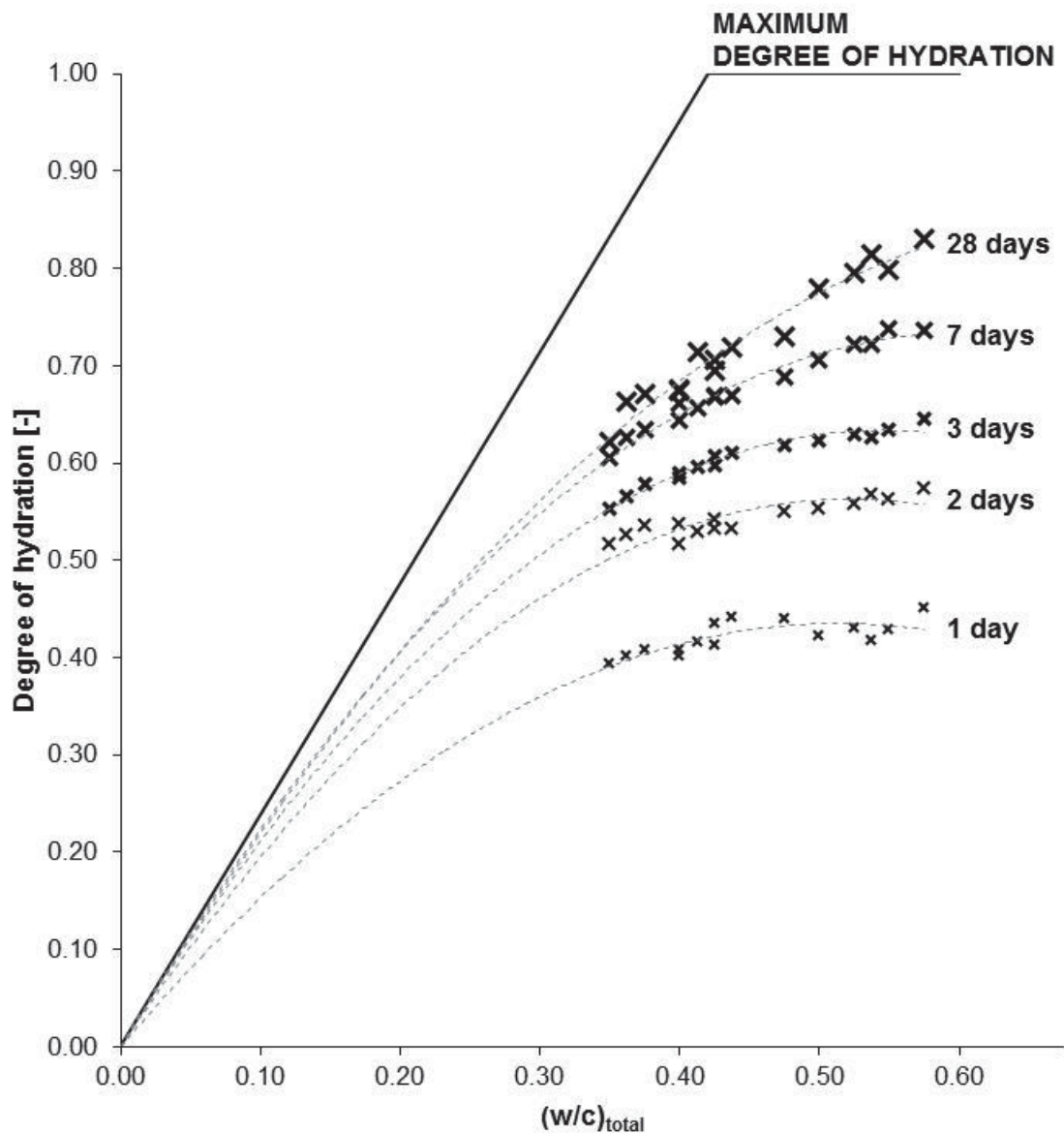


Figure 6: Degree of hydration vs. $(w/c)_{\text{total}}$ at different ages for results from [4]. Maximum degree of hydration according to Powers' model is also shown.

In [4] it was concluded that there is no observable effect of SAP addition for w/c ratio between 0.35 and 0.50, 1-2 days after mixing. When plotting degree of hydration vs. total w/c ratio, it can be seen that all measurements are in an interval, where the trend line for 1 and 2 days has almost no slope; for w/c ratios 0.35 and higher, the degree of hydration at early ages is rather insensitive to w/c ratio.

1 The reason why there is no effect of SAP addition at early ages is probably that there is sufficient
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3 water in the paste.
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8 From 7 days and later, the present study and [4] show the same general trend. There is a mild
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10 accelerating effect of SAP addition for all 3 w/c ratios, when SAP is added with extra water. It is
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12 noteworthy that there also is an effect of SAP addition for w/c ratio 0.50, even though there is
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14 enough capillary water for full hydration without internal curing. The reason why SAP also
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16 increases degree of hydration for $w/c = 0.50$ at this stage may be that the bottleneck of the hydration
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18 process is solubility of various substances [12], and more substance can be in solution, if there is
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20 more free water in the paste system. There is more free water in mixtures with SAP, if water from
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22 SAP fills the “empty” space created by chemical shrinkage within the hydrating paste, and thereby
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24 SAP can increase the rate of reaction. This supports that SAP is continuously emptied and capillary
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26 pores are fully saturated until SAP is completely emptied, as assumed in figure 1.
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35 The results for the reference mixes without SAP agree well with other results in literature, e.g. a
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37 literature review of the influence of w/c on hydration kinetics reported in [13] and an experimental
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39 study reported in [14]. In the later, Bentz et al. use isothermal calorimetry to measure the heat
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41 release during hydration of cement paste up to seven days after mixing. The cumulative heat
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43 release, normalised by the mass of cement in the sample, can be used to predict the degree of
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45 hydration at any time during the measurements. Measurements are made for cement pastes with w/c
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47 ratios ranging from 0.325 to 0.425. The measurements show overlapping curves during the first 12
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49 h of measurements, but then the hydration slows down for paste with lower w/c compared to paste
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51 with higher w/c . The authors point to the supply of free water as the limiting factor for the hydration
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rate. In this light, it is expectable that SAP addition can accelerate hydration, if the SAP addition leads to a significant increase of the amount of free water in the system.

5.2 Chloride migration coefficient

Figure 4 shows that the chloride migration coefficient depends on age, i.e. the chloride migration coefficient decreases as the age increases. The chloride migration coefficient also decreases as the w/c ratio decreases. A factor that combines w/c ratio and age is the so-called gel space ratio, defined by Powers [15]. The gel space ratio X , is defined as the volume of gel solid relative to the space available for it, the latter being equal to the sum of volumes of gel solid, gel water, capillary water and pores created by chemical shrinkage, see equation 5:

$$X = \frac{V_{gs}}{1 - V_{uc}} = \frac{(1 - 64 \cdot 10^{-6} \cdot \rho_c + 0.23 \cdot (\rho_c / \rho_w)) \cdot (1 - p) \cdot \alpha}{1 - (1 - p) \cdot (1 - \alpha)} \quad (5)$$

where the symbols are identical to those used in equations 1a-1e.

In figure 7, all measured chloride migration coefficients are plotted against the gel space ratio calculated from the associated degree of hydration.

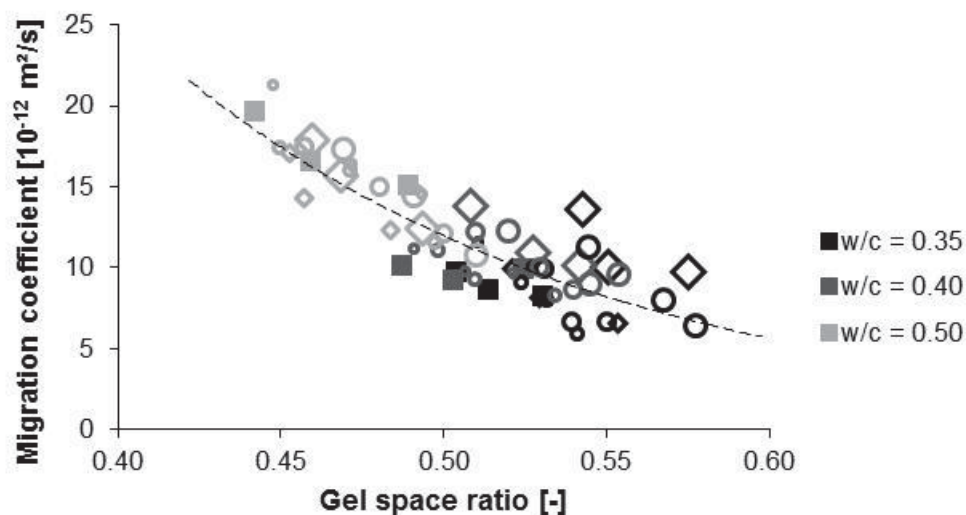


Figure 7: Chloride migration coefficient D_{nssm} vs. gel space ratio (same legend as in figure 3).

In figure 7, the data points are scattered around a trend line. In NT BUILD 492, it is stated that for reproducibility the coefficient of variation is 13 % for concrete with pure Portland cement and higher for concrete with silica fume, so for a migration coefficient of $20 \cdot 10^{-12} \text{ m}^2/\text{s}$, the variation is $\pm 2.6 \cdot 10^{-12} \text{ m}^2/\text{s}$. In the present study, the uncertainty is probably a little higher, because measurements of the migration coefficient are carried out at early ages, and as specimens are water saturated, they continue to hydrate during the experiment. On top of that, there is the uncertainty associated with the gel space ratio, which again is related to the uncertainty of the measured degree of hydration. Therefore, even for a true relation between gel space ratio and migration coefficient, a correlation much better than what is shown in figure 7 cannot be expected. Such a relation seems reasonable, as the capillary pore volume decreases and the tortuosity of the cement paste increases, when the gel space ratio increases.

From this, the conclusion is not a general statement, where SAP addition in all cases lowers the chloride migration coefficient, it is a conditional statement. The first precondition for reduced

chloride transport is that SAP addition increases the gel space ratio, compared to a mix without SAP.

As regards concrete service life, the transport properties at later ages, i.e. 28 days, are generally more important than at very early ages. In that perspective, SAP addition without extra water improves the resistance against chloride ingress in all cases, as this lowers the initial w/c ratio in the cement paste, and that unambiguously increases the gel space ratio. If SAP is added with extra water to account for the absorption, SAP addition only improves the resistance against chloride ingress, if it sufficiently improves the degree of hydration. This is only the case for w/c ratio lower than 0.42 and only up to a certain SAP addition, where all the water absorbed by SAP can be used for cement hydration, if not taking the mild accelerating effect of SAP described in section 5.1 into account.

In figure 7, for w/c ratio 0.50 there are no signs of a systematic trend, where concrete without SAP has higher chloride migration coefficient than concrete with SAP or vice versa. But for w/c ratio 0.40 for equal gel space ratios, it seems that concrete with high SAP additions (large circles and large diamonds) have higher migration coefficients than concrete without SAP or with lower SAP addition rates. This is even more pronounced for the w/c ratio of 0.35. This may be the sign of a “void effect”, where water-filled SAP voids act as direct routes for ion transport; for a w/c ratio of 0.50, the maximum SAP addition of 0.6 % of cement mass equals a void volume of 3.4 % of the concrete volume, for a w/c ratio of 0.35 the SAP void volume is 4.1 %, so the effect should be more pronounced, the lower the w/c ratio. Moreover, the mixtures with the lower w/c ratios also have the highest air void volume (in the fresh concrete, the air content is up to 2.8 %). Therefore, the second precondition for reduced chloride transport obtained by SAP addition is that the effect of increased

gel space ratio is not overshadowed by the effect of increased void volume. In the present discussion, it is presumed that all empty voids (capillary voids, SAP voids and air voids) become liquid filled during the vacuum saturation procedure of the test method. This assumption has not been verified. It could have been investigated, if the mass gain during vacuum saturation had been registered, and the mass gain then was compared to the void volume according to the mix design.

It must be emphasized that the results presented here regarding the influence of gel space ratio and SAP void volume are only relevant in the situation of completely saturated concrete (which is also the precondition for diffusion according to Fick's 2nd law). If the SAP voids are air-filled, they may, contrary to the above mentioned statement, have an effect, where they reduce chloride ingress, because they make up an obstacle that the chlorides cannot travel through. And as the amount of free water will be less in concrete without SAP than in concrete with SAP, this most likely also has an effect on transport. So for a partially saturated concrete, it is not known if the effect of SAP addition will be to promote or to hamper transport.

5.3 Comparison to observations in literature

As mentioned in the introduction, measurements of transport properties for concrete with SAP are rather sparsely reported in the literature. However, SAP is not the only means to achieve internal curing. Pre-wetted lightweight aggregate is another example. Though lightweight aggregates typically only hold water equal to a fraction of their mass [16], and not several times their mass as SAP, they can be used to reduce self-desiccation and autogenous shrinkage in a similar way. And for some concrete properties, e.g. resistance to chloride ingress, the influence of saturated lightweight aggregates (LWA) is better documented than the influence of SAP:

- Bentz [17] studied chloride ingress in mortars with a w/c ratio of 0.40. The control mixture was prepared with normal-weight sand while internal curing ($w_e/c = 0.08$) was provided via pre-wetted fine lightweight aggregates in a second mixture. Specimens were immersed in 1 M chloride ion solution and the chloride ingress was measured after 28 days and 56 days of exposure using a silver nitrate spray technique. The chloride ingress was significantly smaller for mortar prepared with LWA than for the control mortar.
- Liu et al. [18] compared normal weight concrete with a w/c ratio of 0.38 with 4 mixtures containing LWA. The normal weight aggregates were divided into 4 size fractions. In one LWA mixture, the coarsest size fraction of the aggregates was substituted with saturated LWA of similar size. In the next LWA mixture, the 2 coarsest size fractions were replaced, and so on. In general LWA mixtures showed results comparable to what was measured for normal weight concrete, except for the mixture with 100% LWA. In a salt ponding test this mixture showed slightly increased chloride transport. The authors noted that the absorption capacity of the fine LWA (0-1.18 mm) was uncertain, so the w/c ratio of this mixture was uncertain too.
- Zhutovsky and Kovler [19] tested 3 high performance concrete mixes (w/c ratios 0.21, 0.25, and 0.33) with and without internal curing in the form of vacuum-saturated fine LWA. Comparison of results from tests according to ASTM C1202 did not show a general trend. For w/c ratio 0.33, the charge passed was lower for the concrete mixture with internal curing, whereas for the lower w/c ratios internally cured and non-cured mixtures showed similar results.
- Thomas and Bremner [20] investigated chloride ingress for concrete that had been placed at the US Corps of Engineers marine exposure site at Treat Island for 25 years. Concrete mixtures were produced with varying water/binder ratios and varying slag contents, and

parallel mixtures were prepared with coarse normal-weight aggregate and coarse LWA, respectively, whereas the fine aggregate in all cases was a normal-weight sand. The water/binder ratio and binder composition were vital for the chloride ingress, whereas it seemed unaffected by the type of coarse aggregate.

- Di Bella et al. [21] made parallel measurements of chloride transport in plain concrete ($w/c = 0.39$) and internally cured concrete, where saturated fine LWA holds extra water (25 kg/m³ concrete). The measurements were performed with 5 different methods, including NT BUILD 492 and a chloride ponding test. The chloride migration coefficient is measured according to NT BUILD 492 28, 56, and 91 days after mixing. At all ages, the migration coefficient of the internally cured concrete was slightly lower than the migration coefficient of the plain concrete (15-30% lower). The general pattern of the results from the other test methods was also that internal curing reduces chloride transport, but the magnitude of the effect of internal curing depended on the test method.

The overall picture can be summarised: It is not unequivocal if internal curing by pre-wetted LWA reduces or increases chloride ingress, but the sum of results incline towards that there may be a reduction. If internal curing by LWA shall have an effect on chloride ingress, it has to be introduced as fine LWA, probably because only then the major part of the paste phase is close to an internal reservoir. According to Bentz [17], the potentially reduced transport of chlorides in LWA mixtures may be attributed to two different reasons: The interfacial transition zone surrounding a LWA particle is less porous than the interfacial transition zone of a normal-weight aggregate particle and the enhanced degree of hydration due to internal curing leads to a general densification of the cement paste.

1 There is no contradiction between what is registered for LWA and results of the present study.
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3 Internal curing with SAP leads to finely dispersed reservoirs, which in size and number are
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5 comparable with what is obtained with fine LWA. The experiences with LWA support that internal
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7 curing can lower the chloride migration coefficient, when internal curing leads to increased degree
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9 of hydration in mixtures, where the initial w/c of the pastes are equal. The effect of SAP is probably
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11 mainly due to a less permeable gel structure, as SAP addition will only have a very small effect on
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13 the interfacial transition zones.
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17 18 19 20 **6. Conclusion**

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22 Measurements of chloride transport shows that for chloride transport in fully saturated concrete,
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24 internal curing by SAP reduces chloride ingress, if the SAP addition results in an increased gel
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26 space ratio. This is the case:
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32 • if SAP is added without extra water to account for absorption, so that the initial w/c ratio of
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34 the cement paste is reduced
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38 • if SAP is added with extra water to account for absorption and this entrained water
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40 sufficiently increases the degree of hydration. At later ages (28 days at 20 °C or later), this is
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42 generally true, if the w/c ratio is below 0.42, and the SAP addition is adjusted so that the
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44 SAP voids are emptied before the maximum degree of hydration is reached.
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50 The results seem to agree well with results obtained by using pre-wetted lightweight aggregates as
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52 internal curing medium. However, in some of the papers concerning lightweight aggregates, the
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54 effect of internal curing that reduces chloride transport is attributed to the improved quality of the
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interfacial transition zones. The results in this study point out that another effect of internal curing is due to a general densification of the paste phases as expressed by their increased gel space ratio.

In this study, focus has been on how SAP addition influences transport properties, but the study has also revealed that SAP addition has a mild accelerating effect on cement hydration, when extra water is added to compensate for SAP absorption in the fresh concrete mixture. Measurements indicate that hydration is controlled by the total w/c ratio, not the initial w/c ratio of the cement paste.

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